PB-245 756

PESTICIDE POLLUTION STUDIES

Public Health Service
Atlanta, Georgia

March 1963

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Progress Report

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

PESTICIDE POLLUTION STUDIES

Progress Report

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Water Supply and Pollution Control
Region IV, Atlanta, Georgia

March 1963

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INTRODUCTION

The Pesticide Pollution Project of the Division of Water Supply and Pollution Control, Public Health Service, U. S. Department of Health, Education, and Welfare began in 1959 as a result of multiple stimuli which focused attention on the vital need for information concerning the impact of pesticides on water quality. These stimuli include reports of pesticide caused fish kills, the recovery of DDT from surface waters in various parts of the country, and public reaction to the fire ant eradication activities of the U. S. Department of Agriculture. In addition, scientists concerned with the occurrence of carbon chloroform extractables in water have long pointed to the need for more precise and definitive characterization of these materials. In general, the pesticides are a part of this group of organic materials.

The administration and field activities of this Project are directed from the Atlanta Regional Office of the Department of Health, Education, and Welfare. Until July 31, 1962, analytical services were performed under contract by Clemson College, Clemson, South Carolina. Since that date, these activities have been carried out in the Project's own laboratory in Atlanta.

This report of the Pesticide Pollution Studies covers the period from inception of the project in 1959 to February 1963. It will be immediately clear to the reader that this is an informational report only, not to be considered part of the scientific literature, but rather a progress report to keep interested persons informed. Major findings are set forth without presentation of complete data. Some conclusions are tentative and subject to change and many of the detailed analyses are not complete.

During the next few months, formal and fuller publication will be made in the technical literature of the individual study projects described in this report. It is requested that in the meantime the information here not be quoted, cited, abstracted, or reprinted in scientific literature.

Persons wishing to receive reprints or pre-publication copies of future papers should address:

Regional Program Director
Division of Water Supply and Pollution Control
Public Health Service
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SAMPLING AND ANALYTICAL METHODS

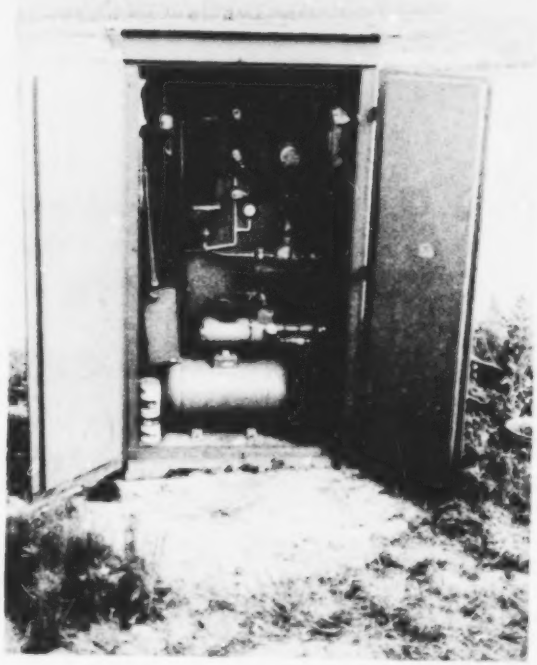
At the start of the project, the methods available for pesticide analysis required relatively large quantities of the material to be identified. Since normal concentrations in water were too small to permit use of whole water samples a concentration technique, the carbon adsorption method of sampling, was adopted. This technique was applied by the then more or less standard practice of passing about 5,000 gallons of water through the filter at a rate of ¼ to ½ gallon per minute.

The methods available until recent months for pesticide analysis, and those which were used during the term of the Clemson contract, consisted of infrared spectrophotometry, paper chromatography, fish bioassay, and a variety of colorimetric analyses. Recent developments in gas chromatography have permitted the application of this technique to pesticide identification and the Atlanta Project now uses it.

Carbon adsorption sampling leaves much to be desired. While quasi-permanent installation is desirable, portable equipment has been developed for use at some locations. The latter is bulky, expensive, subject to mechanical failure and vandalism, and thus limited in its use. A major limiting factor of the carbon adsorption sampling technique is the long time required for collecting a sample. Also the scientist is unable to determine if the recovered material was collected throughout the sampling period, or at one or a group of discrete occurrences.

Admittedly the carbon adsorption technique is but a semi-quantitative tool. The optimum water volume that constitutes a sample remains obscure. Recoveries of pesticides by the carbon from the water and by the solvent from the carbon are extremely variable. In addition, some pesticides are not adsorbed by carbon. Therefore, results obtained by this method must be expressed as quantities recovered rather than as absolute quantities present in the water, and any attempt at determining a material balance utilizing hydrologic studies and depending on the carbon filter method of sampling is of questionable value.

The recently established Atlanta laboratory is equipped with two relatively new analytical devices. One is a microcoulometric titration gas chromatograph developed specifically for the analysis of halogenated pesticides and the organophosphate insecticides containing sulphur. The other is also a gas chromatograph but of different manufacture, using an electron capture detection system. The latter has more general usage and roughly 1,000 times greater sensitivity than the microcoulometric system. Its full potentialities will be investigated after completion of major laboratory operations directed at re-analysis of all samples collected during the life of the Project.



Portable carbon absorption sampling unit equipped with a 3 x 18 inch carbon column, sand filter, and deep well pump.

This new instrumentation relegates earlier analytical methods to a minor and supplemental role in pesticide work. It has substantially reduced the amount of time required for sample processing. Most importantly, perhaps, these new instruments require much smaller absolute quantities of material for detection.

Preliminary studies show promise that a liquid-liquid extraction using as little as one liter of water may provide sufficient residue for a more accurate quantitative analysis than has been available heretofore. This procedure will reduce to hours the processing of analytical data which in the past took up to three weeks.

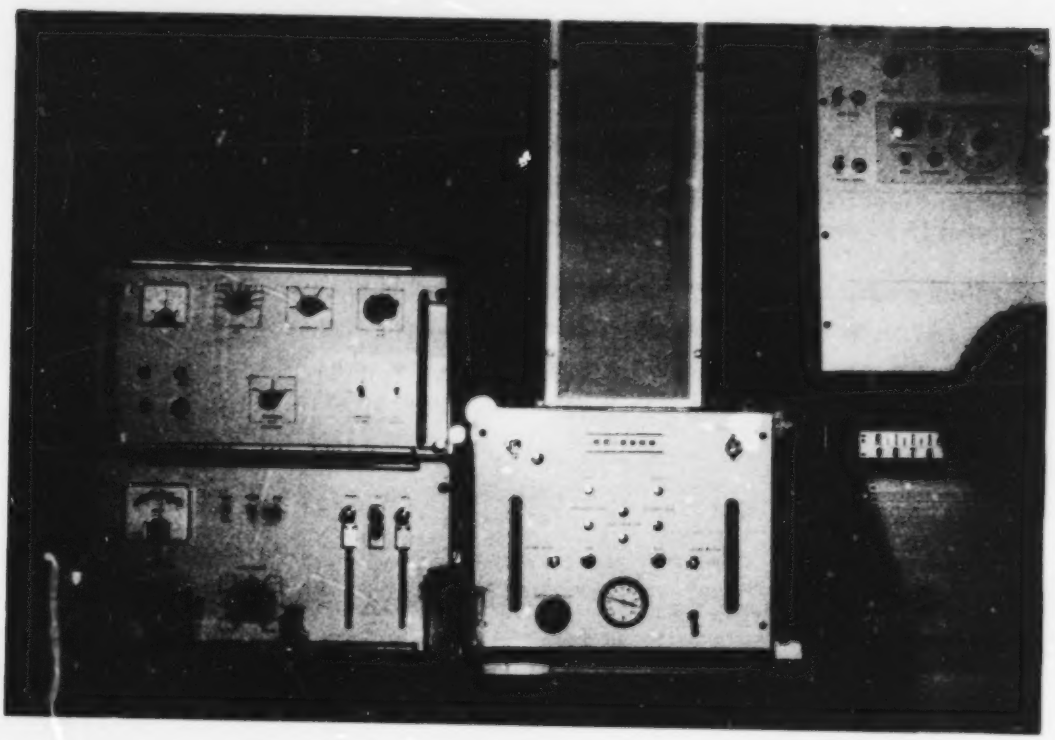
FUTURE ACTIVITIES

This report will refer from time to time to the further development and continuation of certain of the studies reported. These planned operations in the ensuing months will be subject to critical review for appropriateness, results to be obtained, and their contribution to the overall objectives of the pesticide studies.

In general, the Project has operated thus far on the basic philosophy of determining if pesticides used in normal pursuits of man find their way into the water environment. This question can now be answered in the affirmative. The next logical step is to determine why and under what natural circumstances these materials get into the aquatic environment. Several of the studies have investigated this phase and a more exhaustive treatment, particularly in the Flint Creek system, is indicated.

Concomitant with the first phase of the Project, studies have been made to determine if any gross effects of these materials on biological populations in waters could be detected. Generally, such effects have not been demonstrated.

Gas chromatographic system used for detection and measurement of pesticides. The microcoulometric titration cell is at extreme left.



The logical extension of these studies is for the development of information concerning concentration of these materials through the food-chain mechanism and the possible effects on organisms of long term exposure to sub-lethal quantities of pesticides. Work will be initiated on this phase of the Project as rapidly as funds and available staff permit.

FLINT CREEK PROJECT (1959 to February 1963)

The study area is a 400 square mile Northern Alabama watershed drained by approximately 760 miles of stream tributary to the Tennessee River. Flint Creek and the West Fork of Flint Creek are the principal streams in the basin. These two creeks merge a few hundred yards upstream from a conventional water treatment plant drawing water from the stream and serving 5,500 residents of the communities of Hartselle and Flint. The plant receives drainage from the entire basin. The land is generally rolling with some slopes of 15% to 60% in the headwater areas. Soils are loams of limestone or sandstone origin and an estimated 40% of the basin is forested.

Water quality and agricultural practices were investigated from 1959 through 1962. Stream biology was studied in 1959, 1960, and 1962. The most intensive studies were made in the spring, summer, and fall of 1960 by a resident investigator.

Agricultural Practices

Farms in the basin are small with only a very few exceeding 100 acres. Limited diversified agriculture is practiced but cotton is the only crop requiring significant quantities of insecticides. Most of these are applied as dusts by ground equipment, generally from June through mid September. Insecticide usage is probably conservative because of small cotton allotments, and economic and other institutional considerations.

Accurate numbers of cotton farms and acreage in the basin were obtained from the County Agricultural Stabilization and Conservation Offices of the U. S. Department of Agriculture. The extent of insecticide usage by farmers in the water-

Flint Creek Basin showing the sampling stations.

shed was estimated by statistical methods. Each year a random stratified sample was drawn representing 10-17% of the total cotton acreage. The samples were stratified by the fraction of cotton acreage found in the portion of each county that occurred within the basin. Needed information was obtained by personal interview.

The samples were used to estimate the following parameters for the entire basin each year: number of cotton farms using insecticides; mean number of insecticide applications per farm; cotton acreage treated with insecticide; cotton acreage treated with toxaphene, or DDT, or BHC; poundage of individual insecticides used; poundage of individual insecticides used as emulsifiable concentrates; and cotton acreage treated with insecticides formulated as emulsifiable concentrates. Generally speaking confidence limits (0.05) were set on these parameters by using the sample standard error, the Student "t", and a finite population correction term.

In the four year period, 1959-1962, about 15 to 16 thousand acres of cotton were cultivated annually. Estimated area treated with insecticide varied from low of 5,000 acres in 1960 to a high of almost 14,000 in 1962. Minimum usage (58,500 pounds technical) occurred in 1960 and maximum (139,500 pounds) in 1962. Usage estimates in 1959 and 1961 were 85,570 and 99,346 pounds technical, respectively.

Water Quality Studies

Carbon adsorption sampling of raw and finished water was done at the Hartselle water treatment plant from June 1959 to February 1963. The plant provided water treatment consisting of lime-alum coagulation, sedimentation, rapid sand filtration, chlorination, and pH adjustment prior to the spring of 1962 when activated carbon treatment was added. The data presented show toxaphene and BHC were present in raw and finished water throughout the year, every year. Apparently the toxaphene and BHC content of the water was not reduced by treatment.

Some of the results, particularly when apparent differences between raw and finished water samples exist, may be due to artifacts associated with the carbon adsorption sampling method. Therefore, the following discussion is tentative until verified by comparison of results with direct water analyes.

The apparent annual increase in the median recovery of BHC appears to be related to annual usage. For example, lowest recoveries were noted in 1959 and 1960 when usage was moderate to low (3,654 and 2,562 pounds technical, respectively). Similarly, the higher recoveries noted in 1961 and 1962 were associated with increased usage (4,655 and 7,143 pounds technical, respectively). The annual median recovery of toxaphene and DDT does not appear to be related to agricultural usage. The annual usage estimated for these compounds varied from 1959 to 1962 as follows: toxaphene, 37,945-72,066 pounds technical; DDT, 16,762-48,442 pounds technical. In spite of this differential use, toxaphene recovery values were more or less stable from year to year and DDT was never recovered.

Laboratory experiments indicated the following solubilities in water: gamma isomer of BHC, 1.15 ppm; toxaphene, 0.16 ppm; and DDT, 1.3 ppb or less. Therefore, the recovery data seem to support the intuitive assumption that insecticide contamination in water is related to the solubility of the product.

During the summer of 1960 a portable carbon adsorption unit was used to collect samples from eight widely scattered sites on the stream system. All of the samples contained toxaphene and BHC in concentrations in the same order of magnitude as noted at the water treatment plant. Therefore, the insecticide probably originated from the basin in general rather than from a few cotton fields or subwatersheds. Studies are being planned for the future to determine if differential occurrence, within and among kinds of insecticides, in water is somehow related to differential persistence and accumulation of these compounds in terrestrial soils. Similarly, it is planned to make an intensive study of the quantities of insecticides occurring in the major tributaries of the drainage system.

Table I

CONCENTRATION OF BHC AND TOXAPHENE RECOVERED FROM CARBON ADSORPTION SAMPLES COLLECTED FROM FLINT CREEK, ALABAMA, 1959-1962

	Raw Water		Finished Water	
	Parts per trillion			
Year	Median	Range	Median	Range
		BHC		
1959	50	4-210	29	20-70
1960	63	10-217	60	15-200
1961	143	32-1004	123	23-640
1962	188	41-809	320	48-824
		Toxaphene		
1959	41	10-260	59	34-280
1960	41	9-270	55	10-410
1961	39	18-164	37	15-111
1962	37	7-148	44	5-154

The above data represent analyses made on 141 residues including 59 paired raw and finished water samples collected during synchronous sampling periods. All analyses were by microcoulometric gas chromatography.

Biological Studies

Plankton and benthic collections were made at two stations in 1959, seven stations in 1960, and six stations in 1962. Qualitative benthic collections were made in 1959, and qualitative and quantitative samples taken in 1960 and 1962. Quan-

titative plankton studies were made in all years. Semi-quantitative fish collections were made in 1959 and 1960. Most of the biological collections were made during the period June-November. The samples collected in 1959 and 1960 have been completely processed and analyzed. Work remains to be done on samples collected in late 1962.

Zooplankton samples taken in 1959 contained from less than one to 11 individuals per liter. Twenty-four of the 33 samples collected in 1960 contain no zooplankton and the others contained less than one individual per liter. This paucity was attributed to unfavorable environmental conditions such as extreme fluctuations in discharge and high turbidity. Therefore, it was concluded there would have been a scarcity of zooplankton even in the absence of insecticide contamination.

Twenty-four benthic collections, consisting of totals of 158 quantitative samples and 24 qualitative samples, were made in 1960. The macro-invertebrates, except the aquatic worms, were identified to genus. Counts and volumes were determined for the quantitative collections.

The qualitative collections showed considerable taxonomic diversity in both 1959 and 1960. Nineteen to 38 genera of macro-invertebrates, including from 18 to 31 genera of aquatic insects, were noted among the various collections made in 1960. The 1959 collections were essentially the same as those made in 1960. Other organisms frequently noted were snails, clams, crayfish, aquatic sow bugs, and planarians.

Numerically, aquatic insects comprised over 85% of the individuals of 17 of the quantitative collections. Considerable variation was noted among total counts for collections made at various stations and times. At one station the geometric mean of the total count varied from 3 to 39 organisms per ¼ foot^2. At other stations the mean counts were consistently higher and more stable (i.e. 24-45 organisms per ¼ foot^2). Analysis of variance indicated that many of these differences were statistically or highly statistically significant.

The overall quality of the fauna did not suggest that observed reduction in bottom fauna numbers were caused by toxaphene and BHC. The populations showed taxonomic diversity even when depressed. Fluctuations in population numbers appeared to be quite independent of the quantity of insecticide recovered from carbon adsorption samples. In other words, increasing populations were sometimes associated with "high" insecticide recovery and depressed populations sometimes associated with "low" insecticide recovery. Therefore, it was concluded that there was no convincing evidence that insecticide contamination resulted in grossly observable

damage to bottom fauna in the stream in 1959 and 1960.

Fish collections were made at two stations with an electric seine in June and September of 1959 and 1960. The catches before and after insecticide usage in the basin were represented by many size classes and species. The collections contained from six to nine families of fishes representing from 13 to 22 species. The sunfishes were the best represented family (5 to 7 species) in all of the collections. It is very probable that the stream contained a greater taxonomic diversity than indicated by the collections. Visual problems associated with the high turbidity of the stream made the collection of smaller fish (such as the minnows) difficult.

There was additional evidence that the stream system, as a whole, supported a large and varied fish population. Supplemental fish collections made in 1960 with a bag seine in a tributary indicated a fish population similar to that present in the main streams. Anglers with catches of sunfish and catfish were observed in various locations in the fall and summer of 1960.

In conclusion, the Flint Creek system appeared to support a fish population grossly commensurate with the natural environmental conditions present. Because of continuous surveillance it is certain there were no large fish kills in the drainage system in 1959 and 1960 resulting from the normal agricultural use of insecticides.

Fish population studies — Flint Creek, Alabama.

BAYOU TECHE-YOKELY PROJECT (March 1961-January 1962)

In 1961 a study was initiated in St. Marys Parish, Louisiana near the town of Franklin. The Parish is in the coast marsh area and is near sea level. The streams studied were Bayou Teche and Bayou Yokely. Bayou Teche drains over 2000 square miles; however, its precise drainage area in the vicinity of Franklin is indeterminate. Bayou Yokely has a well defined drainage area of 12.1 square miles delineated by a dike and levees formed by the Teche. A gauging station and pump house are maintained at the dike. Ordinarily, water is pumped from the Yokely from one to three times a week depending upon the rainfall. Biological, water quality, agricultural, and hydrological studies were made in 1961 and 1962.

An aerial view of the Bayou Teche-Yokely Study Area in Louisiana.

Agricultural Studies

Soils in the Bayou Yokely drainage area vary from clays, mucky clays, and mixed clays alluvium in the bottom lands to silty, loamy, clayey soils on the higher terraces. Sugar cane is virtually the only crop grown in the Yokely Basin. A total of 3,313 acres of cane is grown in the basin and the average plantation size is 237 acres.

The cane is treated from the air for control of cane borers with clay pellets containing 2% technical endrin by weight. This granular material is applied at a rate of 0.25 pounds technical endrin per acre. In 1961, each plantation made from one to four applications on its entire acreage. In addition, four growers made from one to three partial treatments. A total of 1,959 pounds of technical grade endrin was applied to 3,313 acres in 1961. In 1962, because of poor overwinter survival of the cane borer, only three of the 14 plantations used insecticide. The total usage figure for 1962 is not available at this time; however, it will be substantially less than in 1961.

In 1961, studies were conducted to determine the extent of direct contamination of Bayou Yokely by endrin applied to sugar cane by aircraft. Without notifying the pilots, three groups of aluminum pans (14" diameter) having 5 pans to the group were anchored and floated in the Bayou adjacent to cane fields. Each group was placed one quarter mile apart. Additional pans were placed on the stream bank. Similar experiments were conducted at two other sites in the Parish. In every case no endrin was observed hitting the water during dusting or in the pans after dusting. Therefore, it was concluded direct application was not a significant factor contributing to surface water contamination in 1961.

Hydrological Studies

Rainfall records were obtained throughout the period of study. Six rain gauges, including a continuous recording rain weighing gauge for measuring storm intensity, were located in or immediately adjacent to the Yokely basin. The average daily rainfall has been computed by the Thiessen average area method for June through October 1961. To date, the rainfall records for 1962 have not been analyzed. Pumping records, stage gauge readings, and cross sectional profiles of the Bayou have been obtained from the Parish Engineer. Runoff from the basin has not yet been estimated.

Water Quality Studies

Carbon adsorption sampling stations were established at the down-stream limit of the Bayou Yokely drainage system. Three carbon adsorption stations were associated with Bayou Teche. One sampled raw water at the intake of the Franklin water treatment plant, the second sampled water stored in an open two million gallon holding reservoir prior to treatment, the third was located on a finished water line at the water treatment plant (coagulation, carbon dosing, sand filtration, and chlorination). Continuous operation was maintained during the spring, summer, and fall of 1961. Intermittent operation was in effect in 1962. Bayou Yokely was sampled only in 1961. A portable carbon adsorption sampling unit was used to collect water samples at fish kill points.

Eighteen carbon adsorption samples obtained from Bayou Yokely were analyzed for pesticide residue using microcoulometric gas chromatography. The quantities of insecticide recovered were as follows: six samples contained from 1 to 360 parts per trillion (ppt) endrin; 14 samples contained from 5 to 1,361 ppt dieldrin; and two samples contained from 3 to 4 ppt of an undetermined isomer (s?) of BHC. The median concentration of endrin and dieldrin in positive samples was 101 ppt and 427 ppt, respectively.

Based on County Agent reports, dieldrin was not used for agricultural purposes in the basin from 1960 to 1962. Dieldrin is often applied to soil around building foundations for termite control. The extent of this practice in the basin is being investigated.

Table II shows results of analyses made on carbon adsorption samples of Bayou Teche water. These data, like those obtained from Flint Creek, indicate that conventional water treatment, including the addition of carbon for taste and odor control, is not effective in removing small quantities of insecticide(s) from water.

Table II

CONCENTRATION OF INSECTICIDES RECOVERED FROM CARBON ADSORPTION SAMPLES COLLECTED FROM BAYOU TECHE, LOUISIANA 1961-1962

Compound	No. of samples analyzed	No. of samples containing compound	Median of positive samples	Range of positive samples
			Parts per trillion	
Raw water - pumphouse				
Endrin	22	7	7	1-35
Dieldrin	22	1 (20 ppt)	—	—
BHC[1]	22	10	7	1-73
DDT	22	1 (24 ppt)	—	—
Raw water holding reservoir				
Endrin	21	5	3	1-12
Dieldrin	21	1 (10 ppt)	—	—
BHC[1]	21	10	5	1-42
DDT	21	1 (16 ppt)	—	—
Finished water - treatment plant				
Endrin	18	2	11	2-23
Dieldrin	18	4	3.5	2-16
BHC[1]	18	6	2.5	1-14
DDT	18	1 (5 ppt)	—	—

[1] Undetermined isomer or isomers. Analyses were by microcoulometric gas chromatography.

Biological Studies

Quantitative zooplankton samples were taken at roughly biweekly intervals from March to October 1961 at two stations on Bayou Yokely and one station on Bayou Teche. In 1962, a single collection was made at each station in May, July, and November. In 1961, two benthic sampling stations of 0.5 mile length were established in Bayou Yokely and one station of 0.25 mile length initiated in Bayou Teche. The banks were staked and a grid system established so that predetermined

random samples could be taken. Seven collections were made at each site in the Yokely during the period April-November 1961. Ten quantitative random samples were taken at one station for each collection and twenty at the other. Bayou Teche was sampled by making six collections from June to October 1961. Twenty quanittative random samples were taken for each collection. Qualitative samples were taken every time a quantitative collection was made. The animals, except the aquatic worms, were identified to genus and counted.

All samples have been processed and statistical analyses (analysis of variance) made. Some statistically significant differences were noted among various collections. However, these differences have not yet been correlated with the hydrological and water quality data to determine if they were associated with the presence of pesticide.

A view of Bayou Yokely, Louisiana

HOUMA PROJECT (May 1961-May 1962)

Raw and finished water was sampled by the carbon adsorption method at an industrial water treatment plant. The plant supplies water for a Houma, Louisiana sugar refinery. The water, drawn from Little Bayou Black, was given conventional treatment, excluding carbon dosing. Thirteen raw water and 14 finished water samples were collected from May 1961 to May 1962, except during the period February-April 1962 when the plant was not operating.

Microcoulometric gas chromatography indicated the following recovery of pesticides from finished water: eight samples contained from less than one to four parts per trillion (ppt) endrin; seven samples contained from less than one to 10 ppt BHC [unidentified isomer(s?)]; one sample contained six ppt of 2,4-D (acid equivalent). Similarly, the following recoveries were noted among the raw water samples: four samples contained from less than one to four ppt endrin; and seven samples contained from less than one to 10 ppt BHC.

SPARTANBURG PROJECT (March 1960-February 1961)

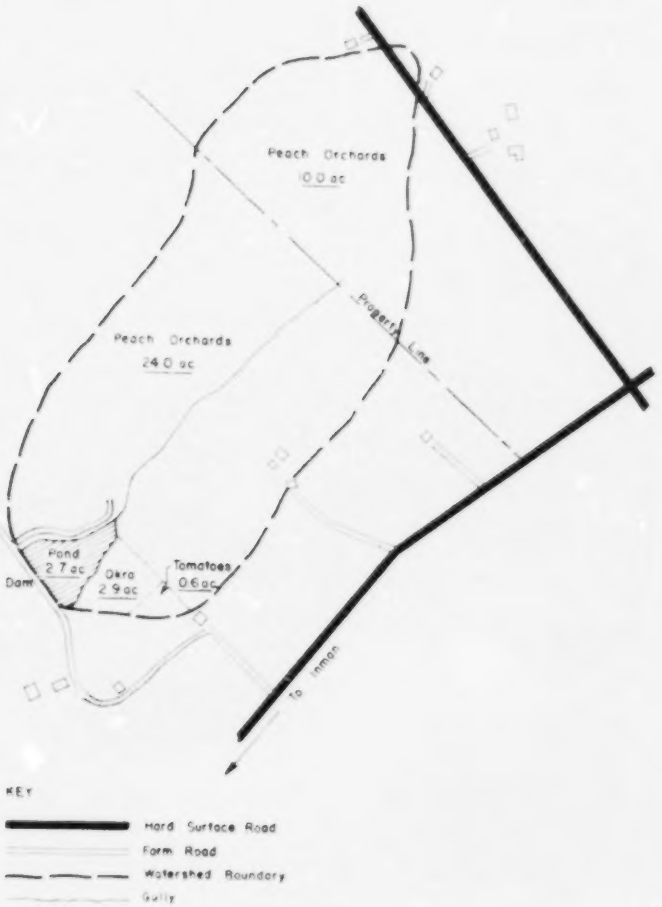
In the spring of 1960 investigations were started in a peach growing area of Spartanburg County, South Carolina. The study concerned a 2.7 acre pond located on a 40 acre watershed where peaches are the principal crop. Insecticide usage information was obtained from the farmers and water, hydrosoil, soil, and biological samples collected. The Averrell-Norris test was used to determine parathion residues in all samples.

Agricultural Studies

The slope of the watershed varies from six to 10 feet per 100 feet. The soil is a sandy clay loam low in organic matter. Surface soil pH varied from 6.7 to 7.1 and samples collected from depths greater than two feet had a pH of less than six.

From April 11 to August 1, approximately 152 pounds of technical grade parathion were applied as a wettable powder to 34 acres of peaches. The average dose was 0.6 pounds technical per acre per application. Other pesticides used were dieldrin, DDT, DDD, BHC, and captan, in amounts minor compared to parathion.

Experimental Watershed near Spartanburg, South Carolina.



Soil Samples

A composite surface soil sample collected in March prior to parathion use in 1960 contained 1.7 parts per million (ppm) parathion. This indicates parathion survival in the soil for a period of at least nine months. Surface soil samples collected from August 1960 to February 1961 contained from 0.23 to 1.39 ppm parathion. Two series of vertical samples taken to a depth of four feet indicated the presence of parathion at depths ranging from one to two feet.

Hydrosoil Samples

A relatively high concentration of parathion (1.9 ppm) was found in pond sediments prior to insecticide use in 1960. Based on the known solubility of parathion in water and the fact that parathion residues were present in the orchard soil (1.7ppm), it was concluded that the parathion entered the pond in association with soil during a period of destructive erosion observed in March. Hydrosoil samples collected in August and November contained 1.13 and 0.09 ppm parathion, respectively.

Water Samples

Parathion was recovered from all water samples collected before, during, and after insecticide use in 1960 (March-December). Quantities, although small, generally increased as the spraying season progressed. The maximum concentration of 1.22 parts per billion (ppb) was recovered in June. A sample collected in December, four months after spraying ceased, yielded the minimum concentration of 0.01 ppb. This was the only sample which also contained DDD and BHC (0.02 and 0.01 ppb, respectively). Observations and the chemical data suggested that spray drift was the most important source of parathion contamination in the late spring and summer.

Biological Samples

Five quantitative benthic collections of 15 samples each were collected from April to September. The animals were identified to genus, counted, and the volume of the sample determined. Thirteen zooplankton samples were collected from April to September. Fish samples were collected by bag seine or gill net in April, August, and September.

Analyses of the biological samples indicated that the aquatic insect, aquatic worm, and zooplankton populations were unaffected by parathion residues in the water and pond mud. However, analysis of variance demonstrated there was a statistically significant reduction in immature aquatic insects associated with parathion use in the watershed. Circumstantial evidence indicates the reduction was indirectly caused by a partial destruction of adult populations in the watershed by ex-

posure to parathion spray and residues. Such destruction would reduce recruitment into the larval population, and hence accentuate losses in aquatic standing crop caused by emergence and fish predation.

(Note: These data are available in published form. See Publication List No. 3 and 4.)

COWEETA STUDIES (May 1961-November 1962)

The Coweeta Laboratory is a 4,300 acre experimental forest watershed maintained by the U. S. Forest Service for the purpose of hydrological research. It is located in the Nantahala Mountains near Franklin, North Carolina. Prevalent vegetation is the typical Appalachian oak-hickory association. The upper watershed is characterized by sharply rising slopes. For example, the elevation drops 1,500 feet in a horizontal distance of about 1.25 miles.

In 1961 and 1962 the watershed was treated with DDT to control elm spanworm. Prior to treatment, a State and Federal interagency committee was formed to evaluate the effects of the spraying. Studies were made of the insect, aquatic invertebrate, fish, bird, and mammal populations before and after spraying. The Public Health Service studied the occurrence of DDT in surface water and the Forest Service provided stream discharge and rainfall data. A carbon adsorption sampling station was established on Coweeta Creek at a site immediately downstream from the watershed.

In 1961, the entire watershed (4,300 acres) was sprayed by fixed-wing aircraft with a 12% DDT oil solution at the rate of one pound technical per acre. In 1962, only 2,100 acres were treated by helicopter with a 6% DDT oil solution at the rate of 0.5 pound technical per acre. The 1962 sprayings were restricted to the ridges and upper slopes. Therefore, only a small portion of the streams received direct application that year. The applications were made in late May of both years.

Carbon adsorption samples were collected from 31 May to 1 August 1961. The study was terminated prematurely because of mechanical difficulties with the sampling equipment. All samples contained DDT residue. The highest concentration of 346 parts per trillion (ppt) was noted in the sample taken during treatment.

Subsequent samples contained consistently lower quantities of DDT. The minimum concentration of 5 ppt was observed in the last sample taken in 1961.

In 1962 samples were collected from mid May to mid October. No DDT was found in the carbon extracts. In these studies the sampling device was modified so that a wool filter cartridge was placed on the water line carrying flow to the carbon cartridge. This was done, in part, to eliminate operating difficulties caused by suspended sediments. It also provided an opportunity to study the possible transport of DDT by suspended materials. The extracts from the wool cartridges containing the sediment are now being analyzed for DDT. To date no DDT has been detected.

DADE COUNTY, FLORIDA STUDIES (March 1961)

In March 1961, the carbon adsorption method was used to sample irrigation wells on three farms in the Homestead area, Dade County, Florida. Much of this region produces winter truck crops such as tomatoes and pole beans. Farming is practiced on a large scale and a single crop may cover a section or more land. The underlying Biscayne aquifer is one of the most productive and permeable non-artesian aquifers in the world. The water table is seldom deeper than ten feet and is near or at the surface during wet periods.

Homestead obtains its water supply from municipal wells. In smaller outlying communities water is supplied by individual home wells drilled to depths of 25 to 50 feet. Frequently, individual home wells are adjacent to or near cultivated fields.

Ground water samples were obtained from six fields. Pesticide usage for a six month period was 15 pounds technical per acre in one field and varied from 50 to 115 pounds technical per acre in the other five. The most frequently used pesticides were: maneb, zineb, parathion, Diazinon, Dyrene, and ethylene dibromide. Lesser amounts of aldrin, heptachlor, DDD, toxaphene, Dibrom, and Karathane were also used.

Analyses were made by fish bioassay, paper chromatography, and infrared spectroscopy. Four of the six samples were negative for pesticides. Paper chromatography indicated the presence of chlordane or toxaphene in two samples. Additional studies in this area are proposed so that possible ground water contamination can be re-evaluated with the new and more sensitive gas chromatographic technique.

Aerial application of pesticides on winter truck crops near Homestead, Florida

HERBICIDE STUDIES (May 1961-February 1963)

A study is being conducted in connection with the Corps of Engineers Expanded Project for Aquatic Plant Control to determine the persistence of certain herbicides in water and hydrosoils.

Six experimental ponds near Anderson, South Carolina were treated with herbicides selected for possible use in control projects. Pond morphology, bottom type, pH, total hardness, and water temperature were determined and, in some cases, experiments designed to determine the effects of these parameters on persistence. The herbicides used and the doses made were: the iso-octyl ester of silvex (granular) at 3.6 ppm acid equivalent; the butoxy-ethanol ester of silvex (emulsion) at 3.0 ppm acid equivalent; the dimethyl amine salt of 2,4-D at 0.6 ppm acid equivalent; Diquat at 2.5 ppm cation content; Paraquat at 2.5 ppm cation content; the sodium salt of Fenac at 4.0 ppm; and 3-aminotriazole at 1.0 ppm.

Existing chemical methods for 2,4-D, silvex, and Fenac were found unreliable for detecting extremely low concentrations of residue in water. However, after esterification of these compounds, microcoulometric gas chromatography was found to yield reliable, reproducible data for microgram quantities. Adaptation of existing colorimetric methods were found to be adequate for detecting and measuring similarly small quantities of Diquat, Paraquat, and 3-aminotriazole.

These experiments are still in progress. Results, to date, indicate the following persistence in water: both esters of silvex were present 120 days after treatment in the low ppb range; 2,4-D was present 62 days after treatment in a concentration less than one ppb; Fenac was present 19 days after treatment at a concentration of one ppm; Diquat was present 23 days after treatment at 10 ppb; Paraquat could not be detected 10 days after treatment, 3-aminotriazole was present 155 days after treatment at 0.1 ppm. Analyses of the pond mud samples have not been completed.

CHOCCOLOCCO CREEK-COOSA RIVER STUDY (May 1961-June 1962)

In May 1961, at the request of the Alabama Water Improvement Commission, studies were started in a stream receiving wastes from a plant which manufactures parathion and methyl parathion. At that time the manufacturing plant's waste treatment facility (activated sludge type) malfunctioned and about two million gallons of partially treated wastes were pumped into the city sewer over a six day period. The city sewage treatment plant which normally gave the wastes additional treatment, was unable to handle the increased volume. Therefore, about 60% of the sewage consisting of the industrial wastes and domestic wastes was by-passed without treatment into Choccolocco Creek, a tributary of the Coosa River. Allegedly, this caused a severe fish kill in Choccolocco Creek and a less severe kill of small bluegills in the Coosa River.

For chemical and toxicological analysis, samples were obtained of: raw sewage and thickened sludge from the city sewage treatment plant at the time of the kill; treated and untreated wastes from the manufacturing plant obtained immediately after the fish kill; technical grade parathion, methyl parathion, and chloro intermediates. Biological observations were made in Choccolocco Creek one day after the by-passing ceased. A carbon adsorption sampling station was operative at Lay Dam on the Coosa River two days later. Lay Dam is 90 miles downstream from the waste outfall.

Chemical Analyses

The Averrell-Norris test was used to measure the parathion content of the samples collected from the treatment plants.

Waste obtained from the industrial treatment plant contained 234 ppm (untreated) and 13 ppm parathion (treated). It is probable that the industrial treatment plant was not operating at full efficiency when these samples were collected. The untreated influent and the thickened sludge from the city treatment plant contained 4 ppm and 667 ppm parathion, respectively.

Bioassay Results

Fish bioassay (fathead minnows) was used to determine the toxicity of intermediate products which were likely to be present in wastes associated with the manufacture of parathion and methyl parathion. The four intermediates tested were: o-o diethyl and o-o dimethyl chlorothiophosphate, and o-o diethyl and o-o dimethyl mercaptothiophosphate. Based on 48-hour TL_m values the following toxicities were noted: the compounds containing the methyl group were from four to seven times less toxic than methyl parathion and from 100 to 200 times less toxic than parathion; the compounds containing the ethyl group were from two to five times less toxic than methylparathion and from 55 to 125 times less toxic than parathion. Equivalent compounds in the chloro state were about half as toxic as the mercapto state.

Biological Observations

Biological observations were made on Choccolocco Creek at four sites downstream and two sites upstream from the waste outfall. In addition, one of the major tributaries was examined. The upstream stations and the tributary contained a wide variety of macroscopic invertebrates. However, a severe reduction in the taxonomic variety of macro-invertebrates was noted at all downstream sites. The reduction noted was typical of damage associated with the presence of toxic materials.

Carbon Adsorption Samples

Near continuous sampling was maintained at Lay Dam from May 1961 through January 1962. From February to June 1962, samples were taken from one to two times a month. Analyses for parathion were made using gas chromatography with a microcoulometric detection cell. All of the 22 samples collected contained parathion. Quantities recovered ranged from 5 to 184 parts per trillion. Maximum concentration was observed in a sample collected during the week following the fish kill in Choccolocco Creek. Reportedly good fishing for bass and other sunfish was maintained in the Coosa River in 1961 and 1962 despite chronic contamination and a partial kill of bluegills noted in May and June of 1961.

Although evidence suggests that the parathion manufacturer is the source of contamination noted at Lay Dam, this may not be the case. The monitoring at Lay Dam was not sufficient to pinpoint the source of contamination since the river and its tributaries flow through agricultural areas that are possible pollution sources.

AROOSTOOK COUNTY MAINE STUDY (June 1962-February 1963)

The Atlanta pesticide laboratory has been analyzing carbon adsorption samples collected from Aroostook County, Maine as a service to Division of Environmental Engineering and Food Protection, USPHS. These samples were collected from three water treatment plants located in an area of intensive potato farming. Although pesticide usage information is cursory, it is known that large quantities and many kinds of herbicides, fungicides, and insecticides are used. To date, 25 carbon alcohol extractable (CAE) and 25 carbon chloroform extractable (CCE) residues have been received for analysis. Analyses completed include: 14 CCE and 14 CAE residues analyzed for chlorinated hydrocarbons by microcoulometric gas chromatography; 10 CCE and 10 CAE residues analyzed for thiophosphorus insecticides by microcoulometric gas chromatography; all CAE residues examined for herbicides by paper chromatography. Pesticide residues were noted as follows: seven CCE residues contained from two to 21 parts per trillion (ppt) DDT; four CCE residues contained from 19 to 98 ppt parathion; one CCE residue contained 19 ppt Diazinon; two CAE residues contained traces of 2,4-D; and two CAE residues contained traces of Fenac.

The sampling and extraction methods used were not adequate to sample for all the pesticides known to be used by potato farmers in the area. For example, the metallic dithiocarbamates and sodium arsenite do not adsorb on carbon. Similarly, Guthion does not elute from carbon by the usual CAE or CCE extraction procedures.

FORT PIERCE STUDY (June 1962-February 1963)

The Florida State Board of Health requested and obtained from the Atlanta laboratory the loan of portable carbon adsorption sampling equipment primarily to determine the CCE content of certain ground and surface waters being considered as auxiliary supply sources for the City of Fort Pierce. Fort Pierce is in Florida's citrus growing area where surface waters are reputed to receive agricultural drainage. Samples collected were sent to the Region IV laboratory for CCE and pesticide analysis.

Ten samples analyzed to date consisted of raw or finished water samples collected from surface runoff, deep wells, and the municipal water supply system. Microcoulometric gas chromatography indicated the presence of parathion in all samples. Recoveries observed ranged from three parts per trillion (ppt) to 32 parts per billion (ppb). The highest concentration was noted in a raw savannah water sample collected at the water treatment plant. Three deep well samples contained from eight to 28 ppt and a five-well composite contained 11 ppb.

It is anticipated that these exploratory studies will soon develop into a major study because of the opportunity to examine parathion contamination in surface and ground water sources as well as municipal water supply.

PUBLICATIONS

Written for publication by staff members during the period 1959-1963 were:

A. Papers available in the literature:

1. Nicholson, H. P. 1959. Insecticide pollution of water resources. Jour. Amer. Water Works Assoc., 51(8): 981-986.

2. Nicholson, H. P. 1961. Pesticide pollution studies in the southeastern states. Proc. 10th Pacific NW. Symposium on Water Pollution Res., USPHS Reg. IX, Nov. 1961; 19-25.

3. Nicholson, H. P. and others. 1962. Insecticide contamination in a farm pond. I Origin and duration. Trans. Amer. Fish Soc. 91(2): 213-217.

4. Grzenda, A. R. and others. 1962. Insecticide contamination in a farm pond. II Biological effects. Trans. Amer. Fish Soc. 91(2): 217-222.

B. Papers cleared and accepted for publication:

5. Sova, C. R. (In print). Agri-mycin 100 as a control for fin rot in fishes. To be published. Prog. Fish Cult.

6. Nicholson, H. P. (In print). Pesticide pollution studies in the southeastern states. To be published in Proc. 3rd Sem. Biol. Prob. Water Pollution (Aug. 1962). USPHS, RATSEC, Cinn., Ohio.

7. Grzenda, A. R. (In print). Public health aspects of weed control in potable water supplies. To be published in Proc. Southern Weed Conf. (Jan. 1963), Mobile, Ala.

C. Papers cleared and submitted for publication:

8. Teasley, J. I. and W. S. Cox. The use of microcoulometric gas chromatography for analysis of pesticide residues from water samples following liquid-liquid extraction. Submitted for publication in the Journ. Amer. Water Work Assoc.

GSA ATLANTA 63-4597